water pressure in the environment. This situation leads to dehydration at lower temperatures than might be expected.

The residue of partial melting is enriched in Fe–Mg minerals. Pyroxenes and some very stable amphiboles, garnets and other anhydrous materials are common. Rocks of this type are often called granulites and are common in the root zones of old parts of the crust, particularly in Pre-Cambrian shield areas.

4. Prograde and retrograde processes

In part two of this paper we discussed mineral memories and emphasized how important it is to understand when the memory begins to function. In the section above we have suggested, that when rocks are heated and undergo prograde metamorphism, they tend to attain equilibrium states. This is hardly surprising for if we can study comparable reactions in the laboratory (almost always under very wet conditions) then clearly as geological times exceed laboratory times by factors of 10^7–10^8, then reactions should reach equilibrium. But just as rocks are slowly buried, they are slowly uncovered. Why then are the reactions not reversed?

There are two main cases to be considered, those involving wet and dry reactions. In the case of wet reactions it is clear that as the necessary water is lost during the heating cycle, to reverse the reactions it must be replaced at appropriate temperatures. Metamorphism reduces porosity and permeability. There is good evidence that it is much easier for the water to leave (virtually by splitting the rock open) than to return. Certainly, trivial amounts of back reaction can be found in most rocks, but it is trivial because first the water is not available and second, its rates of diffusion into the high grade rock is very slow.

When we consider the second class of reactions involving dry solids and including the numerous cases of polymorphism, these solid-state reactions are very slow because they involve movement of atoms or ions in the solid state. The reactions have very large energies of activation which control the rates of reaction. Equilibrium is much more likely to be attained in response to a rising than to a falling temperature. This type of process can be easily studied in a laboratory and reversibility is normally never achieved if the heating and cooling cycles are of comparable duration. However, an even more important consideration in these reactions is again the presence of an aqueous fluid. Many solid–solid reactions would not occur even in geologic times unless a solvent is present to promote material transport. Most inorganic oxides have quite appreciable solubilities in water at elevated pressures and temperatures. Thus the prograde reaction proceeds when a fluid is present but it does not reverse unless the fluid is still present during cooling. This is generally not the case. Doubtless, there are changes which do reverse, some we are well aware of (e.g. the α–β quartz transition), others we may never be aware of for in many ways the rocks themselves

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guide our thinking on what to study. Some reactions are not reversed except under special conditions and hence point to these same special conditions in nature (see calcite–aragonite below).

5. The controlling variables

Once we have seen rocks and their minerals and the reactions which occur, before we commence laboratory studies we can list some of the variables which must be considered. The crust of the earth rarely exceeds 50 km in thickness; this means that lithostatic or load pressures must rarely exceed 15 kb. Thermal gradients are variable. We know that in some regions some rocks melt at depth, a reaction requiring temperatures of perhaps 1000°C. This is unusual and implies that thermal gradients as high as 20–30°C/km must also be unusual, otherwise most crustal masses would be partly molten at the base all the time. We also know that some common rock types probably never melt in the crust and this confirms our upper limit.

On any long-term basis, the crust is not very strong. It is better considered as a very viscous fluid, with a viscosity exceeding 10^{20} poises. Birch[2] considers that long-term stresses probably rarely exceed 10^2–10^3 bars. They are thus not important relative to load except in very special places such as in an active fault zone. Stress can have important effects in increasing reaction rates in solids but these small natural stresses will not shift equilibrium states drastically. The parameters P–T–P_{stress} define the chemical potentials or free energies of the mineral species in a rock. We normally ignore the stress contribution. Time will tell if this is always justified.

When a gas phase is involved, we need to know the total gas or fluid pressure and the partial pressures of all the species in the gas. So far we have been mainly concerned with pure water but in most rocks we will have partly saline solutions and contributions from other species such as CO_2, O_2, H_2S, HF, etc. Water, CO_2 and salts are by far the most dominant solution species in most cases.

Today, we have apparatus which will allow us to do limited types of experiments over all this crustal range and in some cases much more than this. Shock wave experiments can even produce pressures greater than 10^6 bars, pressures which are encountered at the centre of the earth. We can study phase changes, measure solubilities, reaction rates, etc. There are many measurements we would like to make which are difficult, for example most types of absorption spectrometry. At high P and T in the presence of water, there are few materials not subject to corrosion. But as the need arises, these problems tend to be solved and our knowledge of the physical chemistry of the crust is slowly being extended.

6. Some examples of significant mineralogical reactions

6.1. *Equilibrium between analcime, quartz and albite*

In 1954, Coombs[3] described the mineralogical changes in a very thick pile of